



Fe₂O₃/ZrO₂ an Effective Catalyst for Benzylation of Aromatic Compounds in Green Synthesis of Diphenylmethane and its Derivatives

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ABSTRACT

Diphenylmethane and its derivatives are synthesized in excellent yields at 80°C over ecofriendly catalyst Fe₂O₃/ZrO₂ by benzylation of aromatic compounds with benzyl chloride in short duration. Wet impregnation method was adopted to synthesize the catalyst Fe₂O₃/ZrO₂ and characterized by the techniques like XRD, FTIR, SEM and UV-Vis diffused reflectance spectra. XRD and IR results indicate the presence of mixture of monoclinic and tetragonal phases in pure zirconia whereas only tetragonal phase is observed in Fe₂O₃/ZrO₂ catalyst. Higher catalytic activity of the catalyst Fe₂O₃/ZrO₂ can be correlated to presence of tetragonal phase, higher surface acidity and redox potential. The catalyst can be easily separated from the reaction mixture, recycled and reused.

Keywords: Catalyst; Benzylation; Benzyl chloride; Diphenylmethane; Tetragonal phase

INTRODUCTION

Friedel-Crafts reactions are of great interest due to their importance and widespread use in synthetic and industrial chemistry. Liquid phase alkylation and acylation of aromatic compounds using homogeneous catalysts are the commonly practiced Friedel-Crafts reactions [1,2]. However, conventionally used homogeneous acid catalysts *viz.* AlCl₃, BF₃, H₂SO₄, etc. pose several environmental and technological problems like disposal of spent catalyst, corrosion, difficulty in separation and recovery of desired product, high toxicity, etc. All these catalysts need dry atmosphere and reagents as they are moisture sensitive. In addition to this, degradation, polymerization and isomerization of products arising due to the high acidic nature of these catalysts causes a significant reduction in the expected primary product yield [3-5]. In view of this, active research has been directed at substituting the traditional homogeneous catalysts with environment benign heterogeneous catalysts like zeolites, clay minerals, metal oxides and mixed metal oxides. Development of reusable acid catalysts which show high activity for Friedel-Crafts reaction is thus of great practical importance [6,7].

Various kinds of Lewis acid-promoted benzylation reactions including application in industry have been developed, and especially Friedel-Crafts benzylation reaction is of great synthetic significance in industrial processes [8-10]. On the other hand, many of asymmetric Lewis-acid catalyzed benzylation reactions have also been developed. Benzylated products are important building blocks for the synthesis of many pharmaceuticals, agro-and fine chemicals, for example, piritrexim, trimethoprim, avrainvilleol, papaverine, beclobrate, anastrozole, and letrozole, have been shown to possess interesting biological activity [11-15].

Friedel Crafts alkylation is carried out on AlCl₃ and other Lewis acids [16-19], clays obtained by exchanging the original cations of K10 by Ti⁴⁺, Fe³⁺, Zr⁴⁺, Cu²⁺, Zn²⁺, Ce³⁺, Cr³⁺ and Sn²⁺ cations [20], InCl₃, GaCl₃, FeCl₃ and ZnCl₂ supported on commercial clays or on high silica mesoporous MCM-41[21] mesoporous silica with different Sn, Cu and Ga contents[22,23], Amberlyst-15[24], series of zeolites and metal modified zeolites [25], mesoporous Al/SBA-15 catalysts [26], 3-methyl-1-sulfonic acid imidazoliumtetrachloroaluminate ([Msim]AlCl₄) or silica sulfuric acid (SSA) [27]SiO₂ supported silver [28], niobium phosphates [29] SeCl₄ and TeCl₄ [30], Sulfated tin oxide [31].

The development of new solid acid catalysts which enhance the yield and selectivity towards target product is desirable considering the innovative aspects. Zirconia with different degree of acidity can be synthesized depending on reaction requirement, which makes it potential catalyst for industry devoted to transformation of organic compounds. Several reactions catalyzed by Zirconia based solid acid catalysts is described by Arata and Hino *et al* [32]. Among solid super acid catalysts reported, sulfated zirconia received much attention due to its high activity to catalyze many reactions at low temperature [33]. It is known that mixed oxides often show enhanced acidity, activity and thermal stability than their constituent single oxides [34,35]. Therefore we undertook investigations to prepare solid acid catalysts of Fe⁺³ doped zirconia.

EXPERIMENTAL SECTION

Preparation of ZrO₂

10g of Zirconium oxychloride octahydrate was dissolved in 100ml of distilled water. To the Zirconium oxychloride solution 5N Ammonia solution was added drop-wise under continuous stirring on magnetic stirrer until the solution becomes slightly alkaline. Then the total salt was precipitated as Zirconium hydroxide. The precipitate was filtered and washed with distilled water until it is free from Ammonia and dried in oven at 150°C for 24 hours. The dried Zirconium hydroxide was powdered and calcined at 600°C for about 6 hours.

Preparation of Fe₂O₃/ZrO₂

1.244 grams of Ferrous sulphate heptahydrate was dissolved in 10ml of distilled water and 5grams of powdered Zirconium hydroxide was added to it. Water was evaporated on water bath by continuous stirring. The resultant mixture was calcined at 600°C for 6 hours.

The catalysts prepared were characterized by XRD, SEM, EDS, UVDRS and FTIR.

Catalyst characterization

The powder X-ray diffraction patterns were recorded on XRD 7000 Shimadzu instruments by using nickel filtered CuK_α radiation and scintillation counter detector. The scattered intensity data were scanning range from 10° to 80° by scanning at scan speed of 2.000(deg/min), sampling pitch 0.0200 deg and preset time 60 (sec). Debey-scherrer equation is used to determine average crystallite size of the particle.

Scanning Electron Microscope (SEM) investigations performed on a Hitachi model SEM-EDS S3700N scanning electron microscopy at an applied voltage of 15.0 KV.

FTIR spectra of the catalyst were recorded on a BRUKEROPTICS model: TENSOR 27 spectrometer at ambient conditions. Self-supporting KBr pellets containing the catalyst samples were used to scan the spectra.

UV-Vis diffuse reflectance spectral (DRS) measurements were made using UV-vis spectrophotometer (V650, JASCO) in the range 200–800 nm. BaSO₄ was used as the reflectance standard.

Catalytic activity

In a typical experimental procedure a mixture of simple/substituted benzene (20 mmol) and benzyl chloride (10 mmol) was taken in a 25 ml round bottomed flask and 0.1 g of catalyst was added. The reaction mixture was stirred under solvent free condition at 80°C temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was dissolved in ethyl acetate and the catalyst was separated by simple filtration. The purification of the products was done by column chromatography using pet ether as mobile phase and silica gel (60-120 mesh) as stationary phase. The product samples were collected and the product was collected by evaporating the solvent using rotator-evaporator instrument. The products were identified by comparing NMR, IR spectra of samples with the data which was already reported and the isolated yields were determined.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the as-prepared and calcined samples of pure ZrO₂ and Fe₂O₃/ZrO₂ in the range of 2θ = 10°- 80°.

The pure zirconia calcined at 873K shows XRD patterns with 2θ values at 28 and 31.06 degrees which are corresponding to the presence of the monoclinic phase of zirconia and some reflections corresponding to tetragonal phase of zirconia at 2θ value 29.91 degrees (Figure 1a). The selective stabilization of the tetragonal phase of zirconia depends on several factors like critical crystallite size, and the presence of phase stabilizer either in the bulk or at the surface. The tetragonal phase of zirconia is also stabilized in presence of impurity ions in zirconia lattice [36,37]. Incorporation of Iron on to zirconia lattice imparts a significant influence on the zirconia crystal structure. Figure 1(b) shows the XRD pattern of the tetragonal phase of zirconia (2θ = 30.05°, 34.9°, 50.3°, 60°). In the present study, stabilization of the tetragonal phase of zirconia can be attributed to the existence of dopant such as Fe⁺³ ions in the zirconia lattice which induces oxygen ion vacancy in the crystal

lattice of zirconia which in turn helps in the stabilization of the tetragonal phase. Pure ZrO_2 exhibit mixture of monoclinic and tetragonal phase, whereas Fe^{+3} promoted ZrO_2 stabilizes to the tetragonal phase. The average crystallite size of the samples is almost same. In the present scheme, pure ZrO_2 was very less active due to its moderate acidic strength and Iron promoted ZrO_2 was observed to be more active towards the Benzylolation reaction of substituted Benzenes under solvent-free condition at $80^\circ C$ temperature. Average crystallite size of ZrO_2 and Iron promoted ZrO_2 calculated from Scherrer's formula are 17.82 nm and 20.89 nm respectively. The enhanced catalytic activity of Iron promoted ZrO_2 may be because of surface acidity which is due to charge imbalance between metal ions of the catalyst and may be due to lowering in crystallite size by the incorporation of Fe^{+3} in to the Zirconia lattice. The FT-IR spectra of both pure and Iron modified zirconia are shown in the following figure 2.

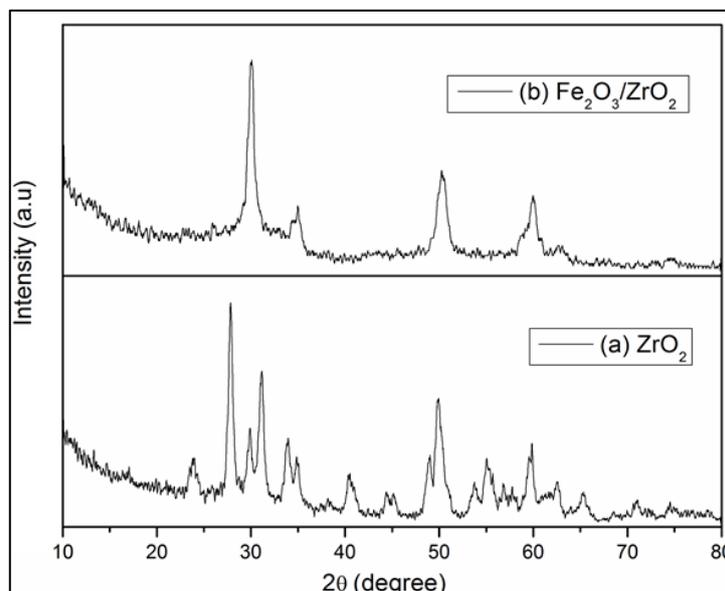


Figure 1: XRD pattern of (a) pure ZrO_2 and (b) Fe_2O_3/ZrO_2 calcined at 873K

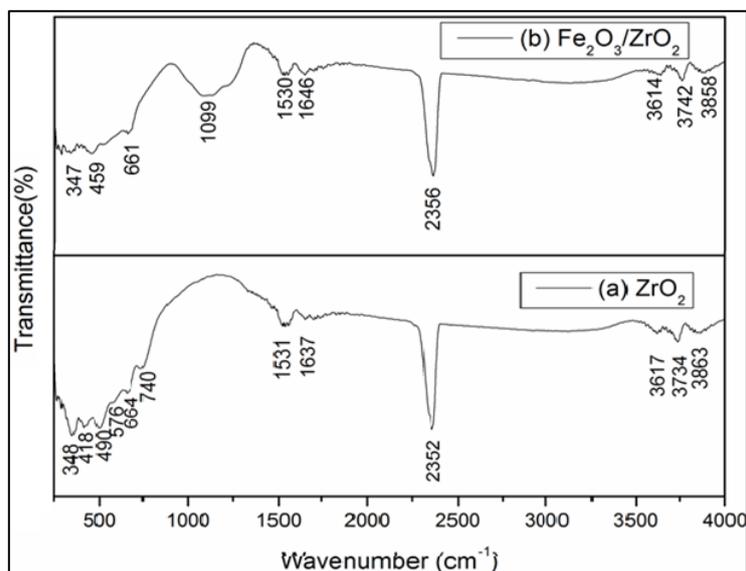


Figure 2: FTIR spectra of (a) pure ZrO_2 and (b) Fe_2O_3/ZrO_2

From Figure 2(a) the absorption bands appear at 348, 418, 490, 576, 664 and 740 cm^{-1} are characteristic vibrations of Zr – O bonds of the crystalline ZrO_2 among which the bands at 576 cm^{-1} and 740 cm^{-1} are characteristic bands of monoclinic Zirconia whereas 490 and 664 cm^{-1} are of tetragonal ZrO_2 . The occurrence of these bands in the present sample indicates the formation of crystalline zirconia phase. The peaks at 1531 cm^{-1} and 1637 cm^{-1} are attributed to symmetric and asymmetric vibrations of C=O bonds respectively. The absorption peak appearing at 2352 cm^{-1} is due to the absorbed atmospheric CO_2 by metallic cations. The peaks in the range of $3600\text{ to }3900\text{ cm}^{-1}$ are attributed to water molecules absorbed by ZrO_2 .

Figure 2(b) shows the FTIR spectra of Iron modified Zirconia. From spectra the characteristic peaks corresponding to the monoclinic phase of Zirconia disappeared and the absorption bands appearing at 459 and

661 cm^{-1} are corresponding to Zr – O vibrations of the t-ZrO₂. This means that the tetragonal phase of Zirconia was stabilized by impregnation of Iron into the Zirconia lattice. Scanning electron microscope images of pure and Iron modified zirconia are shown in the following Figure 3

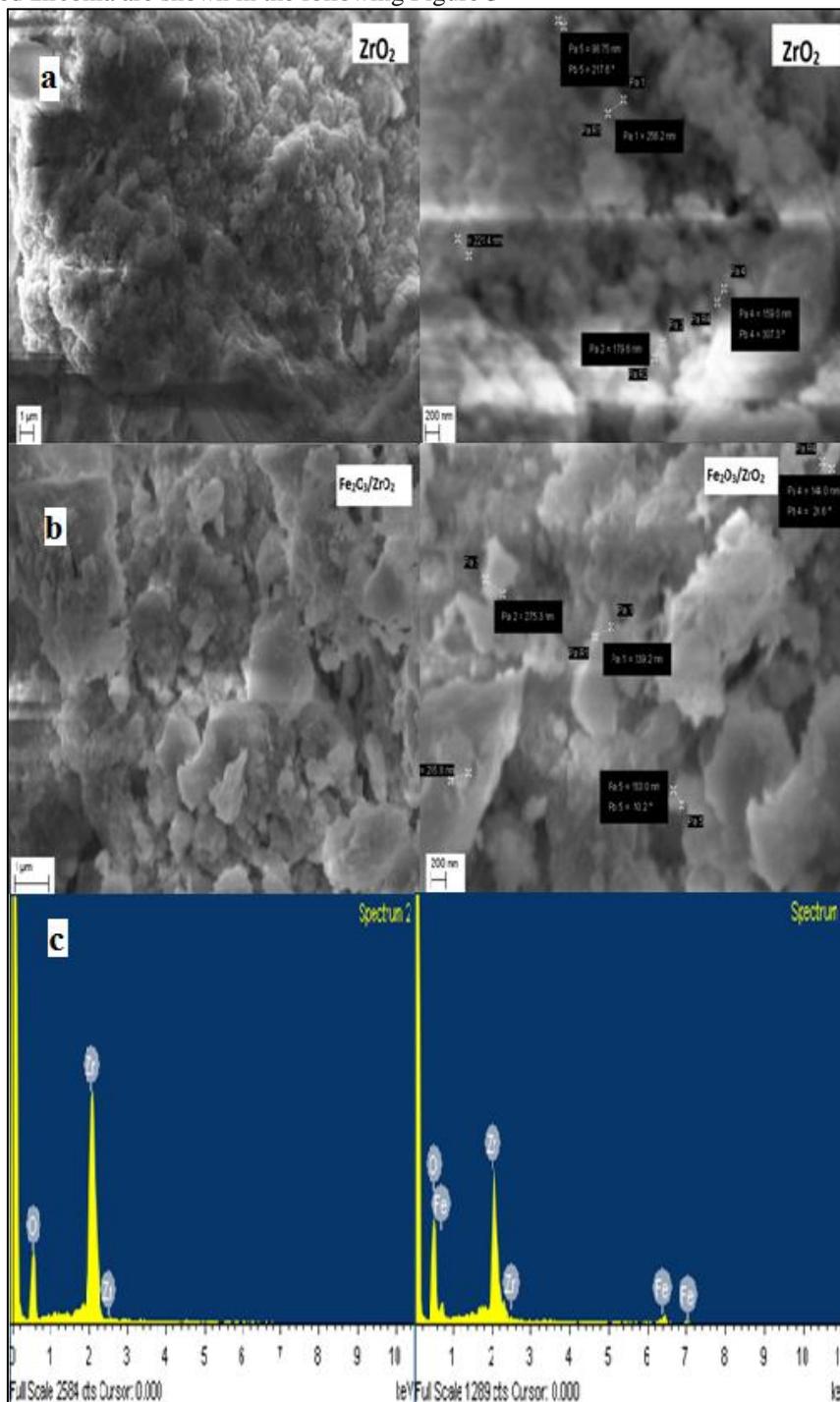


Figure 3: (a) SEM images of pure ZrO₂; (b) SEM images of Fe₂O₃/ZrO₂; (c) SEM images of pure ZrO₂ and Fe₂O₃/ZrO₂ respectively

Figure 3 shows the SEM images of ZrO₂ (3a), Fe₂O₃/ZrO₂ (3b) and EDS (3c) of both the samples. The shape of the ZrO₂ and Iron modified ZrO₂ particles is granular shape. From SEM photographs the average size of ZrO₂ particles is 182 nm and the size of Iron modified ZrO₂ particles is 219.5 nm. There is an increase in particle size due to doping of Fe⁺³ into Zirconia lattice. The same trend was observed in grain size calculated from Sherrer's formula.

Figure 3(c) shows the energy dispersive spectra of both the catalysts which show elemental composition. The EDS of pure Zirconia shows only Zr and O elements whereas The EDS of Iron modified Zirconia shows only Fe, Zr and O elements in their stoichiometric ratio. We did not see the presence of any foreign element in the

compounds. The UV-Vis diffused reflectance spectra of the pure ZrO_2 and $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ recorded in the range 200-800 nm are shown in Figure 4

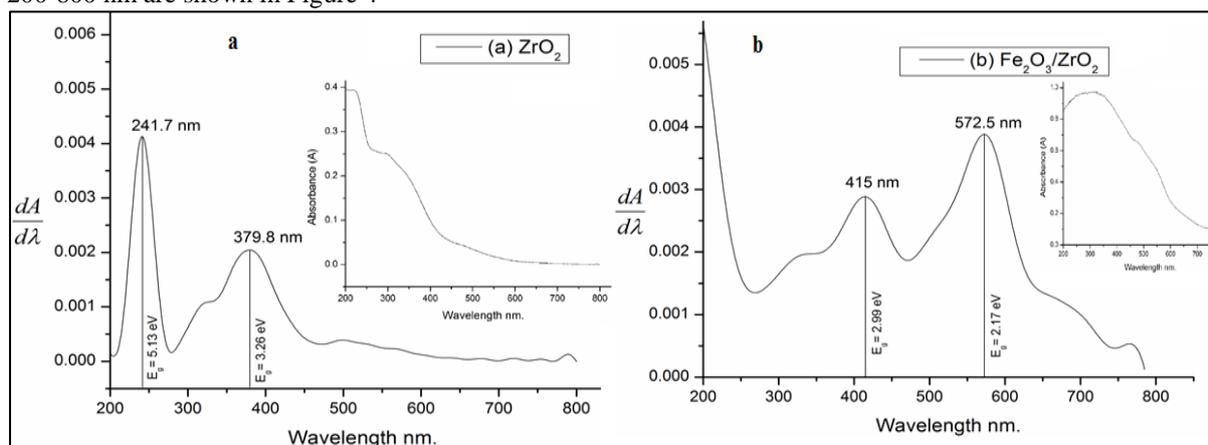


Figure 4: (a): The UV-Vis diffused reflectance spectra of the pure ZrO_2 ; The UV-Vis diffused reflectance spectra of $\text{Fe}_2\text{O}_3/\text{ZrO}_2$.

ZrO_2 is a direct band gap insulator which shows inter band transition in the UV region of the spectrum. The differential plot of UV-Vis diffused reflectance spectra of pure ZrO_2 shows two bands at 241.7 nm and 379.8 nm while the spectra of Iron modified ZrO_2 exhibit two bands, first band shifted to below 200 nm and the second one appears at 415 nm. For the region above 400 nm up to 800 nm there is another strong absorption band at 572.5 nm which is due to doping of Fe^{+3} ions.

Catalytic activity: Friedel-Crafts Benzoylation reaction

The reaction between benzene and benzyl chloride produced diphenyl methane in good yields in shorter reaction time in presence of acidic catalysts. The reaction was monitored under solvent-free condition at 80°C . The reaction was also carried out in presence of the different catalysts under similar conditions. The results are as shown in the table 1.

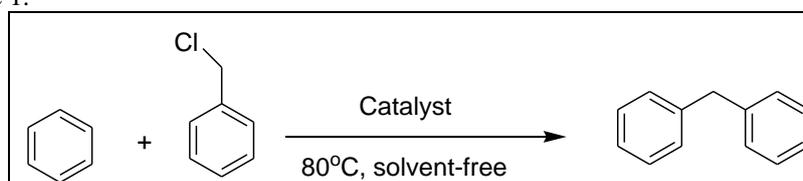


Table 1: Comparison activity of different catalysts towards Benzoylation of benzene by benzyl chloride under solvent-free condition at 80°C

S.NO	Catalyst	Time(min)	Yield(%)
1	$\text{Li}_2\text{O}/\text{ZnO}$	180	0
2	$\text{Al}_2\text{O}_3/\text{ZrO}_2$	150	65
3	$\text{Fe}_2\text{O}_3/\text{ZrO}_2$	30	92
4	ZnO/ZrO_2	40	91
5	ZrO_2	180	0

From table 1 it is clear that $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ is more active than ZnO/ZrO_2 and $\text{Al}_2\text{O}_3/\text{ZrO}_2$. However phase stabilized Zirconia catalysts have shown more activity than pure ZrO_2 . Pure ZrO_2 and $\text{Li}_2\text{O}/\text{ZnO}$ were observed to be inactive (upto 180min) towards Benzoylation of benzene by benzyl chloride under solvent-free condition at 80°C . Though Zirconia has acidic sites, it was inactive in catalyzing the Benzoylation reaction under solvent-free condition at 80°C . There was no reaction in presence of pure Zirconia even after 180min because it is moderately acidic. The acidic strength of Zirconia is too low to catalyze the reaction. To change the physico-chemical properties of Zirconia doping of impurity can be done. Acidic and basic properties of zirconia can be altered by incorporating suitable promoter atom. Impregnation of Fe^{+3} into Zirconia enhances the catalytic activity to the large extent than the other catalysts towards Friedel – Crafts Benzoylation reaction. The reaction was completed in presence of $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ within 30min with the yield above 90%.

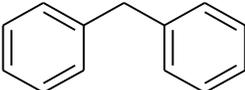
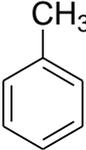
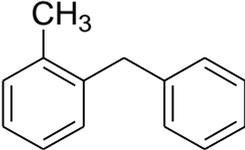
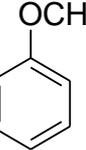
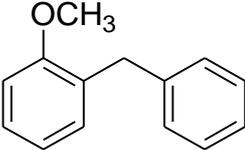
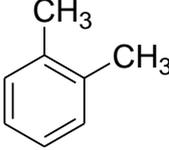
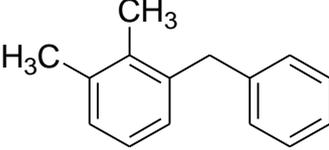
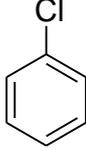
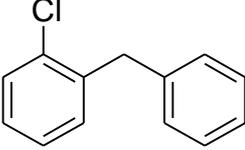
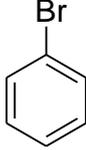
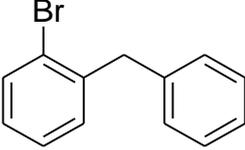
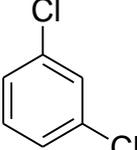
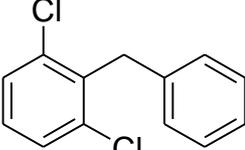
The reaction between benzene and benzyl chloride was monitored under solvent-free condition at different temperatures in presence of $\text{Fe}_2\text{O}_3/\text{ZrO}_2$. The results are tabulated as below:

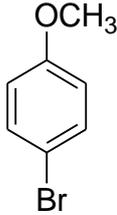
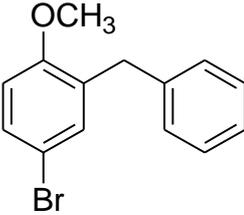
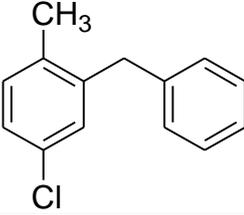
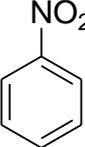
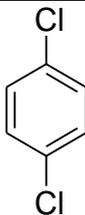
Table 2: Effect of temperature on Friedel – Crafts Benzylation reaction using benzene and benzyl chloride in presence of Fe₂O₃/ZrO₂ under solvent-free condition at 80°C

S.NO	Temperature (°C)	Fe ₂ O ₃ /ZrO ₂	
		Time	Yield (%)
1	25	24hrs	0
2	40	24hrs	0
3	60	05hrs	65
4	80	30 min	92
5	100	12 min	76
6	120	07 min	62

There was no reaction between benzene and benzyl chloride up to 40°C under solvent-free condition in presence of Fe₂O₃/ZrO₂ even after 24hours. Low yield of the product was observed for the reaction at 60°C and above 80°C temperatures. The lower yield of the desired product at higher temperatures is due to further benzylation of mono benzylation product. The reaction was completed within 30 minutes in presence of Fe₂O₃/ZrO₂ with yields above 90%. Therefore the optimum temperature for this reaction is 80°C. All the reactions of substituted benzenes were carried out in presence of Fe₂O₃/ZrO₂. The results are given in Table 3.

Table 3: Benzylation of benzene and substituted benzenes using benzylchloride in presence of Fe₂O₃/ZrO₂ at 80°C under solvent-free condition

S.NO	Reactant	Product	Time(min)	Yield (%)
1			30	92
2			18	91
3			14	95
4			15	90
5			12	94
6			40	80
7			6	92

8			40	89
9			19	93
10		Insoluble solid mass obtained (may be poly benzylated product)	45	-
11		No reaction	-	-

The reaction of benzene and substituted benzenes with benzyl chloride under solvent-free condition in presence of $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ at 80°C gives Diphenylmethane and its derivatives. All the reactions in presence of $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ were completed within 40 minutes with good product yields. The reaction using Chlorobenzene was more active than the other mono substituted benzenes whereas Bromobenzene is least active. While in the case of di-substituted benzenes 1,3-Dichlorobenzene was more active and p-Bromoanisole was least reactive. With Nitrobenzene the reaction was vigorous after 45 minutes. It produces a semi-solid for which the isolation became difficult. However, electron-donating group on benzene facilitate the Friedel – Crafts Benzylation reaction while electron withdrawing group decreases the reactivity of benzene ring. 1,3-Dichlorobenzene was more active whereas 1,4-Dichlorobenzene was inactive towards Friedel – Crafts Benzylation reaction under solvent-free condition in presence of $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ at 80°C .

The catalyst from the first run was collected by simple filtration. It was washed with pet ether and dried at room temperature. The resultant $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ catalyst was reused for the next run under similar conditions. There was no appreciable change in their activity for the next two runs also.

CONCLUSION

The following conclusions were made: 1) $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ was prepared by wet-impregnation of Fe^{+3} on $\text{Zr}(\text{OH})_4$ particles and this is followed by calcination at 873K. 2) XRD pattern and FT-IR data reveals that pure ZrO_2 crystallized in the mixture of monoclinic and tetragonal phase whereas $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ stabilized to tetragonal phase. 3) Impregnation of Fe^{+3} into Zirconia enhances the catalytic activity to the large extent than the other catalysts towards Friedel – Crafts Benzylation reaction under solvent-free condition at 80°C . 4) $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ was more active probably because of creation of more active sites on the surface of the catalyst due to (a) lower particle size, (b) charge imbalance between metal ions (c) difference in redox potentials of metal ions. 5) The catalyst can be re-used. 6) The products were obtained with good yields and were identified by comparing the ^1H NMR and FTIR spectral data with literature.

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